



Evaluation of mechanical and thermal properties and creep behavior of micro- and nano-CaCO₃ particle-filled HDPE nano- and microcomposites produced in large scale

Harun Sepet¹ · Bulent Aydemir² · Necmettin Tarakcioglu¹

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Abstract

The influence of the interfacial area and the particle size of CaCO₃ filler particles on the mechanical and thermal properties of high-density polyethylene (HDPE) was studied in this work. The HDPE-based nano- and microcomposites were manufactured by using an industrial compounder system. The tensile, impact, creep, flexural and hardness properties of the filled and unfilled HDPE samples were investigated. The experiment revealed that the addition of both micro- and nanoparticles increased the tensile and flexural modulus of unfilled HDPE. However, it was observed that the addition of these particles did not have a significant effect on the tensile and flexural strength of unfilled HDPE. On the other hand, the presence of these particles decreased the elongation of break of unfilled HDPE. The impact strength of filled HDPE composites decreased slightly with both micro- and nanoparticle contents. The nanoparticle at high stress level (16 MPa) is more effective on the creep behavior of unfilled HDPE than on microparticles. However, microparticles were found to be more effective at low stress levels (8 and 12 MPa). It was found that the particle size has a profound effect on the thermal and physical properties of unfilled HDPE, such as density, melt flow index and vicat softening temperature. The results showed that the size of filler particles has a significant effect on the mechanical and thermal properties of the unfilled HDPE. Therefore, the size selection of constituent materials of nano- and microcomposites is an important consideration because it directly affects the functional performance of particle-filled HDPE nano- and microcomposites.

Keywords HDPE · CaCO₃ · Filler particle size · Creep · Mechanical properties · Thermal properties

✉ Harun Sepet
harunsepet@selcuk.edu.tr

¹ Department of Metallurgy and Materials Engineering, Technology Faculty, Selçuk University, Konya, Turkey

² TUBITAK National Metrology Institute (TUBITAK UME), Gebze, Kocaeli, Turkey

Introduction

High-density polyethylene (HDPE) is one of the most popular thermoplastic polymers used in the world. There have been important applications of HDPE in the industrial area due to its good performance, surface smoothness, easy processing, low plasticization time and low cost. It has been successfully employed in industrial applications, such as heavy load ropes, liquid storage tanks and mechanical parts running under load. In the polymer industry, inorganic fillers are added to the thermoplastics to improve the mechanical properties and reduce the cost on the final product. Conventionally, polymers are filled using micron-sized CaCO_3 particles. The CaCO_3 , which is a filler particle, can be used in many industrial areas, such as pigments, paints, coatings, plastic, paper, food, cosmetics and rubber. Furthermore, CaCO_3 fillers are widely used as a cost-reducing filler for costly thermoplastic resins. Therefore, CaCO_3 filler size has been the subject of research for large-scale mixtures. For this research topic, the CaCO_3 filler particles may be considered to optimize the properties of an HDPE-based nano- and microcomposite.

A narrow size distribution, uniform shape and definite crystal structure are important features for the fillers used in industrial production. These features of CaCO_3 particles play a crucial role in modifying the thermal and mechanical properties of the filled polymers [1]. Particle size, particle content and particle/matrix interface adhesion have significant effects on the mechanical properties of micro- and nanoparticle-filled polymer composites [2]. Bartczak modified HDPE by three different sizes of CaCO_3 particles of 3.50 μm , 0.70 μm and 0.44 μm weight average diameter in various volume fractions. Tensile and creep properties of CaCO_3 filled HDPE were investigated as a function of filler particle size. The large filler particles (3.50 μm) brought stronger increase in the modulus than those with smaller particle sizes (0.70 μm and 0.44 μm) to HDPE filled with CaCO_3 particles [3]. Sahabian investigated thermodynamic parameters of unfilled HDPE and 10 wt% CaCO_3 -reinforced HDPE nanocomposite using DSC and TMA tests; also the authors demonstrated that the creep properties of HDPE nanocomposites reinforced with different nano-sized CaCO_3 depend strongly on CaCO_3 content [4, 5]. Lorusso probed the effect of filler particles with different shapes and sizes on thermal and mechanical performance of rigid polyurethane foams. They emphasized that the contribution to mechanical behavior of elongated filler is better than the spherical filler [6]. Chen surveyed the effect of particle size on damage dissipation in polymer filled with nanoparticles. They determined debonding energy criterion. This criterion means damage dissipation is strongly dependent on the size of particles regarding to the macro properties of the unfilled polymeric materials [7]. Fu investigated extensive study on the effects of particle size, particle/matrix interface adhesion and particle loading on the stiffness, strength and toughness of polymer composites [2]. The particle size differences within particle-filled polymers influence mechanical behavior of polymer matrix. This effect reveals as dissipation mechanisms, such as shear bands, particle debonding and plastic voiding. These mechanisms may be

Table 1 Physical properties of micro- and nano-CaCO₃ particles

CaCO ₃ type	Color	Density (g/cm ³)	Surface area (m ² /g)	Particle size	Oil absorption (%)
Nano-sized	Ultra white	2.95	28	50–100 nm	35.34
Micron-sized	White	2.70	1.7	~2.5 μm	17

Table 2 Chemical composition of micro- and nano-CaCO₃ particles

Composition	CaCO ₃	MgO	SiO ₂	SO ₃	Fe ₂ O ₃	BaO
%	99.26	0.19	0.13	0.08	0.04	0.30

the basic reason for the mechanical behavior [8–10]. Chen discussed the effects of different wood particle sizes and particle mixture ratios on the properties of wood–plastic composites produced in laboratory conditions because of the cost of industrial production [11]. Thio investigated the mechanisms of deformation and fracture of CaCO₃-filled isotactic polypropylene (iPP) [12]. In addition, they demonstrated that the iPP matrix module and J-integral for static loading of iPP were improved by adding three different CaCO₃ particles [13]. Dusunceli investigated that stiffness, elastic modulus, vicat softening temperature, melt viscosity, density of industrial HDPE nanocomposite are improved significantly with the addition of 10 wt% nano-sized CaCO₃ particles, but it decreased the tensile stress at break, impact strength and Shore D hardness [14]. It has been shown that dramatic improvements and deterioration in mechanical properties can be achieved by incorporation of 10 wt% of nano-sized CaCO₃ particles in HDPE matrix.

In this study, the effect of particle size was investigated by using a single filler (10 wt%) ratio due to the high cost of industrial production. In addition, this filler ratio was commonly investigated in CaCO₃-filled polymer nano- and microcomposite studies [15–19].

The market demand for functional particle-filled polymer has rapidly increased in recent years. It is necessary to investigate the positive and negative effects of filler particle size on the functional properties of polymer composites. The aim of this study is to report experimentally the mechanical and thermal behavior of industrial HDPE-based composites, associated with filler particle size.

Material and methods

Materials

Polymer Marketing Company Limited, Thailand, supplied the HDPE used in this study. The nano-CaCO₃ (trade name: adaCAL-N1-C) and micro-CaCO₃ (trade name: adaCAL-B1) particles pre-treated with stearic acid (or quaternary ammonium) were

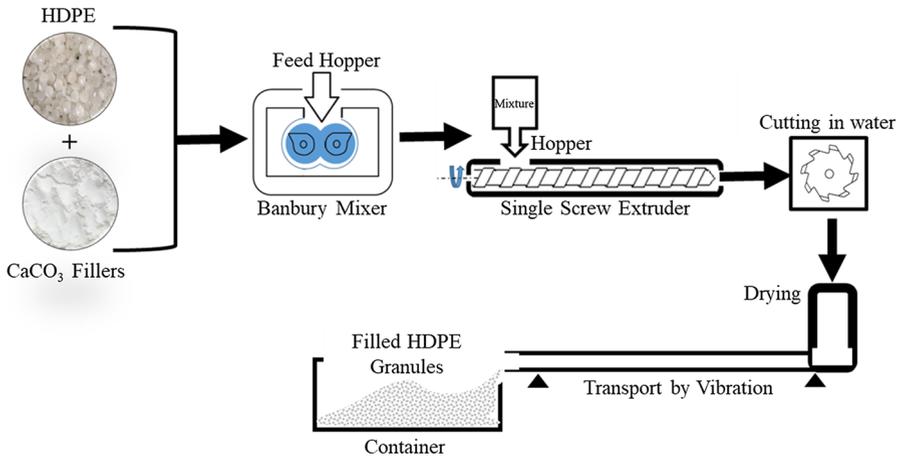


Fig. 1 The scheme of manufacturing process

Table 3 Mixing ratios of unfilled HDPE and micro- and nano-CaCO₃ particles-filled HDPE samples in large scale

Components of nanocomposite	Sample codes		
	Unfilled HDPE	Micro-CaCO ₃ /HDPE	Nano-CaCO ₃ /HDPE
Micro-CaCO ₃ particle, kg/wt%	0/0	10/10	–
Nano-CaCO ₃ particle, kg/wt%	0/0	–	10/10
HDPE, kg/wt%	100/100	90/90	90/90

provided from Adacal Co., Turkey. The physical properties and chemical compositions of CaCO₃ filler particles are given in Tables 1 and 2, respectively.

Manufacturing of polymer nano- and microcomposites

The micro- and nano-CaCO₃ particles-filled HDPE composite granules were prepared by the melt-mixing method using compounder system, which consists of industrial banbury mixer, single-screw extruder and granule cutting. The scheme of manufacturing process is illustrated in Fig. 1. The mixing ratios of nano- and micro-composite ratios are presented in Table 3. Then, the HDPE mixtures containing micro- and nano-CaCO₃ particles were taken into the hopper of the banbury mixer. Then, the hot nanocomposite mixture was transported by conveyor to the extruder when it reaches 180 °C. The nano- and microcomposite hot mixtures received from the extruder are cut into granules when it comes out of the reflector. Then, it is centrifuged and cleaned of water drip. Then, it was taken off by using a fan and conveyed to the container. The nano- and microcomposite granules were molded as

plate using an injection-molding machine with a melt temperature of 210 °C, mold temperature of 65 °C and injection pressure of 50 MPa. The molded samples were conditioned at 23 °C for 24 h before further testing [14, 20].

Determination of mechanical properties

The tensile tests were performed by using a universal testing machine with a load capacity of 50 kN at test speed of 50 mm/min. The stress, strain and modulus were calculated according to ASTM D638. The flexural strength and secant modulus of samples were measured using a three-point bending test according to ASTM D790. The three-point bend fixture, manufactured by Shimadzu, was used in a universal test machine running in a three-point bending mode. The tests were carried out with a span-to-depth ratio of 16:1 at a test speed of 1.3 mm/min. At least five samples were tested for each sample group, and the results were averaged. Impact strength of samples was evaluated using Zwick impact testing machine with 2.0 J pendulum hammer according to ISO 179. The tensile, bending and impact tests were performed at 25 ± 3 °C in the humidity of $30 \pm 20\%$. All impact samples had V-notches with 0.1 radius. At least ten samples were tested for each sample group. The creep tests were conducted with a Zwick Z250 model tensile testing machine at the National Metrology Institute in the Scientific and Technological Research Council of Turkey (TUBITAK). The test parameters were adjusted with the software called TestXpert, and the test results were calculated with this software. All creep tests were performed at 23 ± 1 °C and $50 \pm 10\%$ humidity. The samples were gripped by jaws and applied to preload. Then, extensometer was automatically attached to it and remained on throughout the entire test. At least three samples were tested for each sample group. The Shore D hardness measurements were implemented according to the ASTM D2240 standard with six replicates for each of the samples. The samples used all test were cut from injection-molded composite plates using a cutting die.

Determination of physical and thermal properties

The density of the samples was measured at the room temperature using liquid pycnometer method according to ISO 1183. The melt flow rates of the samples were determined using a Zwick polymer test melt indexer, at 190 °C using a 10 N load and a dwell time of 10 min according to ASTM D1238. Vicat softening temperature (VST) values of samples were performed using an Instron HDT 3 model vicat thermal tester, at 10 °C/min heating rate, using a 10.03 N load according to ASTM D1525. Five samples were tested in each sample group, and the average value was reported.

Electron microscopy (SEM and TEM) and X-ray diffraction (XRD) Characterizations

The fracture surface of samples was coated with gold sputtering for better visibility with a cressington sputter coater 108 at 5–7 nm thickness at 0.18 mbar. The SEM

images of tensile and impact fracture surface were taken with a Zeiss Evo 10 testing machine under accelerating voltage of 30 kV. Transmission electron microscopy (TEM) (FEI, Tecnai G2 Spirit BioTWIN model) was used to specify the particle size and morphology, dispersion and distribution of nano-CaCO₃ in the HDPE matrix. The XRD patterns of micro- and nano-CaCO₃ particle-filled and unfilled HDPE samples were obtained using a Panalytical X'pert powder diffractometer. Nickel-filtered Cu K α radiation (radiation wavelength, $\lambda=0.154$ nm) was produced by an H3R X-ray generator at an operating voltage of 45 kV and a current of 40 mA. The scanning angle, 2θ , for all the experiments was kept between 1° and 35° with a step size 0.004°.

Results and discussion

Mechanical properties

The tensile strength, elastic modulus, elongation at break, flexural strength, flexural modulus and impact strength of filled and unfilled HDPE matrixes were measured and are listed in Table 4. The stress curves of filled and unfilled HDPE matrixes are shown in Figs. 2 and 3. The incorporation of both micro- and nano-sized filler particles enhanced the modulus of HDPE as shown in Table 4. The tensile modulus of the HDPE matrix improved considerably with the decrease in the size of the filler particle. These results, depending on the size of the filler particle, are consistent with those reported in literature [21–24]. Sumita et al. [23] reported that the nanoparticles present higher tensile modulus and strength than microparticles to the polymers. The highest tensile modulus of the HDPE with the addition of nano-CaCO₃ particles rather than micro-CaCO₃ particles into the HDPE matrix was reached. The reason for this increase may be attributed to the huge interface area between nano-sized filler and matrix. At the same reinforcement ratio, the total surface of nanoparticles is much larger than microparticles. Provided that, the interfacial debonding takes place for all fillers (micro and nano sized) dispersed in the matrix, nanoparticle-filled HDPE matrix leads more energy dissipation comparing to microparticle-filled HDPE matrix because of the interfacial debonding [7]. According to this information, the size effect of filler particle is important on the tensile strength and modulus of the filled HDPE. On the other hand, the highest flexural modulus of the HDPE was found to be 913.2 ± 58.2 MPa with microparticle added into the HDPE matrix. The flexural properties of the filled HDPE increased significantly with larger-sized filler particles; Chen et al. [11] reported on a similar tendency on different wood particle sizes filled HDPE composites. The strength is strongly dependent on the stress transfer between the particles and the matrix [25]. The microparticle/matrix interface adhesion is stronger than that of nanoparticle under flexural stress (simultaneous tensile and compression), and the stress applied to the microparticles can be attributed to the effective transfer of stress between particle/matrix. In cases where high nano- or microfiller particle content could not be well dispersed and distributed in the polymer matrix, clustered filler particles may reduce tensile strength of the polymer matrix. Tensile strength of polymer matrix with high CaCO₃ content

Table 4 Tensile properties of unfilled HDPE and micro- and nano-CaCO₃ particle-filled HDPE

Samples codes	Tensile properties		Flexural properties			Impact properties	
	Ultimate tensile strength (MPa)	Strain (%)	Elastic modulus, $E_{%5}$ (MPa)	Flexural strength (MPa)		Flexural modulus, $E_{b%0.8}$ (MPa)	Impact strength (kJ/m ²)
				Flexural strength (MPa)	Flexural strength (MPa)		
Unfilled HDPE	19.45 ± 0.68	700 ^a	266.4 ± 18.1	23.88 ± 1.2	497.5 ± 42.8	28.86 ± 3.69	
Micro-CaCO ₃ /HDPE	19.10 ± 0.40	542.6 ± 190	271.1 ± 11.5	22.86 ± 0.9	913.2 ± 58.2	23.58 ± 4.27	
Nano-CaCO ₃ /HDPE [14]	19.43 ± 0.42	247.3 ± 48.5	279.8 ± 8.1	23.18 ± 0.7	746.6 ± 43.1	19.77 ± 2.25	

^aNo rupture

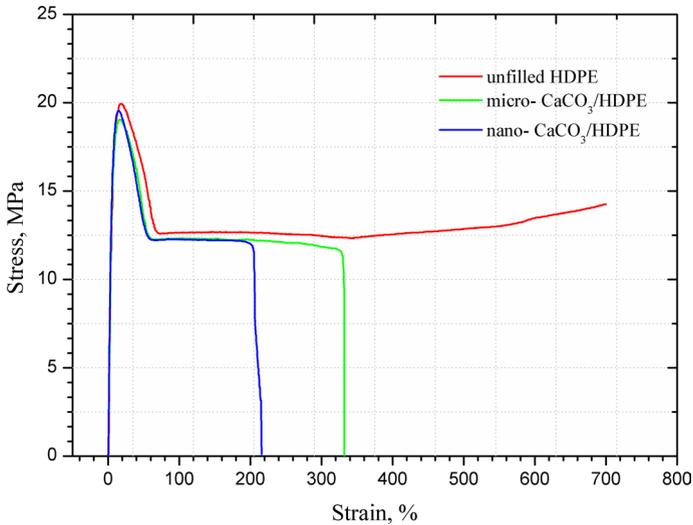


Fig. 2 The tensile stress–strain curves of the unfilled HDPE and micro- and nano-CaCO₃ particles-filled HDPE

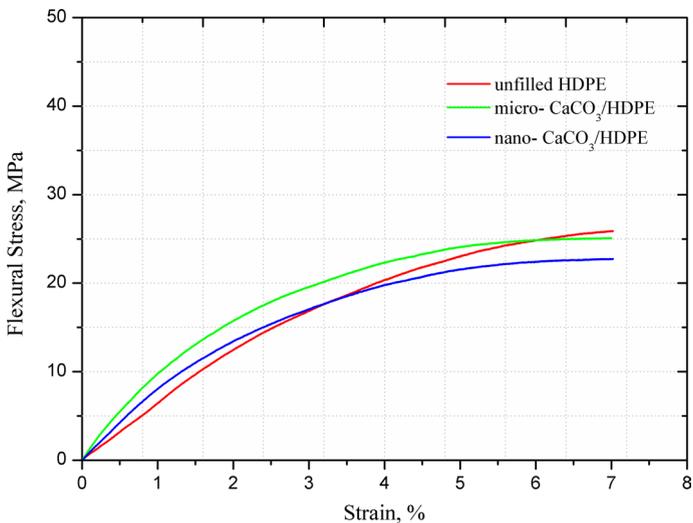


Fig. 3 The flexural stress–strain curves of the unfilled HDPE and micro- and nano-CaCO₃ particles-filled HDPE

reduces due to agglomeration [14, 26]. In Fig. 9a, the number of clumped nanoparticles is very low. Therefore, the tensile and flexural strength almost remained unchanged with the addition of 10 wt% micro- and nano-CaCO₃ particles. It can be found that elongations at break of filled HDPE samples decrease substantially, compared with that of unfilled HDPE. Dai Lam et al. reported similar results on

elongation at break of the filled polypropylene composites [24]. It was found by our previous work that the impact strength decreased with the nano-CaCO₃ particle content, falling to about 32% of that of unfilled HDPE at a nanoparticle content of 10% by weight [14]. The impact strength of 10 wt% micro-CaCO₃-filled HDPE composite is higher than that of nanoparticle/HDPE nanocomposite. However, both micro- and nanoparticle contributions significantly reduced the impact properties of unfilled HDPE. This crucial decrease in the impact strength is shown in Table 4. It was detected from morphological observations in Figs. 11 and 12 that micro- and nanoparticles lead to the cavitation [27] and weak stress field interaction [28] around the particles.

Creep properties

The creep tests were carried out at different stress levels, 8 MPa, 12 MPa and 16 MPa for 600 s at the strain rate of 1E-4 1/s for creep behavior ascertainment of the unfilled HDPE and filled HDPE. The notable numerical data for the creep tests are extensively presented in Table 5. The stress-strain creep curves at different stress levels are given in Figs. 4, 5, and 6, respectively. As outlined in Table 5, the maximum creep strain (ϵ_m) and strain drop ($\Delta\epsilon$) increased with the stress level change from 8 to 16 MPa. This result including all the samples, as mentioned in the Dusunceli [13] and Aydemir [29], is related to delayed response of the polymer chains. The size of filler particle, adhesion surface, surface characteristic and contribution amount are considered to affect the mechanical behavior of the filled polymers [30, 31].

The creep test results showed that the presence of filler particle improved the creep behavior of unfilled HDPE matrix. However, the micro- and nanoparticles provided different effects at different stress levels in the creep tests. It was found that the microparticles are effective at low stress levels (8 and 12 MPa) on the creep behavior of unfilled HDPE matrix, while nanoparticles at high stress level (16 MPa) are effective. A restricted interfacial adhesion effect occurred between nanoparticle and polymer chains owing to low ϵ_m value at low stress levels. In other words, the microparticles have considerable interactions with polymer chains at low stress levels due to their larger particle size during creep deformation as compared to the nanoparticles. The microparticles lead to a more restricted polymer chains mobility than nanoparticle at low stress levels. The stretched linear polymer chains under the tensile load approach each other within the appropriate critical distance, and polymer chains' interval reduces. In this case, the size of the filler particles remaining in between the polymer chains becomes significant. In low ϵ_m value, the adhesion between the filler particle/polymer chain increases when the microparticles are squeezed between the polymer chains. The nanoparticle may create this effect at high stress levels, thanks to its nanosize. As it is shown schematically in Fig. 7, the decrease in filler particle size at high stress levels increase the adhesion surface between filler/HDPE matrix. The creep test results proved that the nanoparticle, which has a larger interfacial area at high stress level, is better than microparticle with reinforcing effect due to interfacial adhesion effect.

Table 5 The maximum creep strain value (ϵ_m), strain drop ($\Delta\epsilon$), absorbed energy (W) of filled and unfilled HDPE samples at 8 MPa, 12 MPa, 16 MPa stress levels

Samples codes	Creep properties at different stress levels									
	8 MPa			12 MPa			16 MPa			W N mm
	ϵ_m (mm)	$\Delta\epsilon$ (mm)	W N mm	ϵ_m (mm)	$\Delta\epsilon$ (mm)	W N mm	ϵ_m (mm)	$\Delta\epsilon$ (mm)	W N mm	
Unfilled HDPE	1.86±0.01	0.93±0.01	216±1	3.74±0.3	2.00±0.20	648±29	8.08±0.4	4.95±0.3	1683±69	
Micro-CaCO ₃ /HDPE	1.56±0.02	0.80±0.01	171±5	3.26±0.1	1.88±0.02	509±18	7.87±0.7	5.20±0.6	1436±76	
Nano-CaCO ₃ /HDPE	1.60±0.30	0.83±0.04	176±4	3.33±0.1	1.90±0.06	526±11	7.16±0.1	4.56±0.1	1389±70	

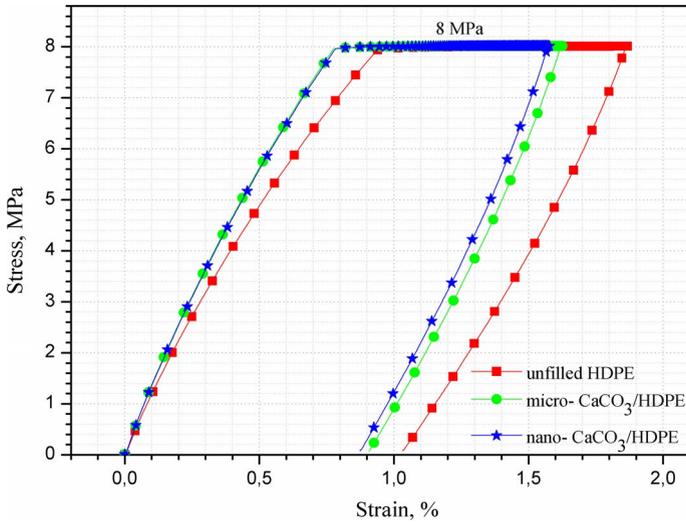


Fig. 4 The curves of stress–strain on 8 MPa stress level

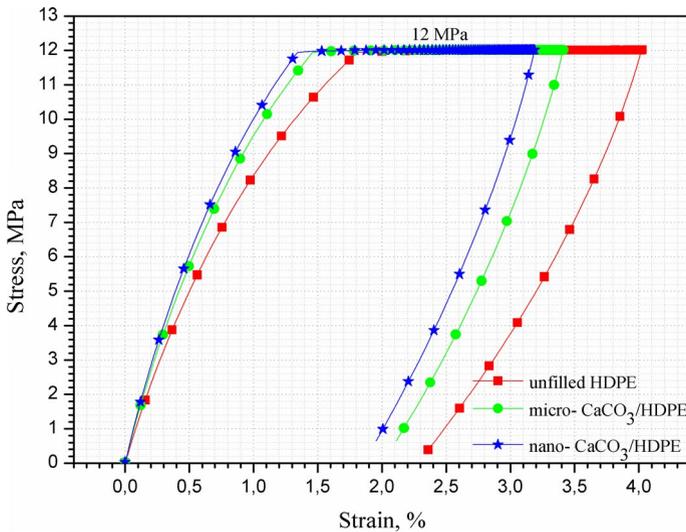


Fig. 5 The curves of stress–strain on 12 MPa stress level

Generally, the absorbed energy (W) is defined as the area under the curve of stress–strain. It can be detected from Figs. 4, 5, and 6 that the total amount of absorbed energy increases with change in the stress level. It was found that the W increased about 8 times for the filled and unfilled HDPE when the stress level was changed from 8 to 16 MPa. The W that can be expressed as the deformation ability decreased with the addition of filler particles during the creep test. The W

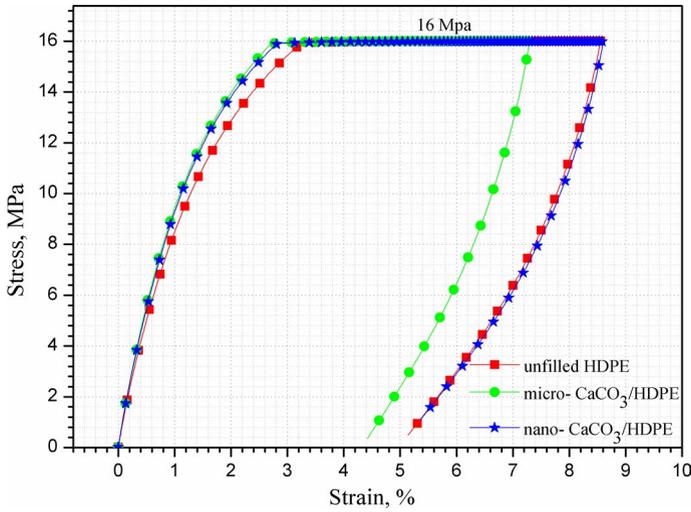


Fig. 6 The curves of stress–strain on 16 MPa stress level

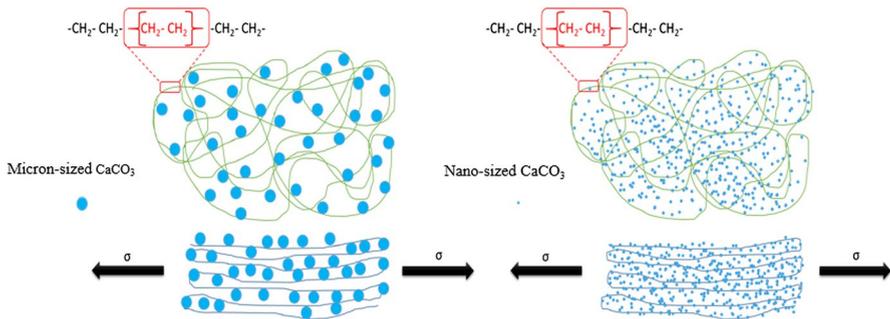


Fig. 7 Schematic illustrations of the interaction with the particles/polymer chain in the semicrystalline polymer under high stress. The spherical solid symbols and the green line represent the dispersed particles and the high-density polyethylene chains, respectively

of microparticle-filled HDPE was less than the nanoparticle-filled HDPE at low stress levels. Nanoparticle fillers were more effective in reducing the amount of energy absorbed at high stress levels. This result which is observed in nanoparticle-filled HDPE attributed that the dissipation energy [7] required for interfacial debonding is less.

Physical and thermal properties

The physical and thermal properties of the filled and unfilled HDPE matrices were measured, and the results are given in Table 6. The density of unfilled HDPE, nanoparticle/HDPE and microparticle/HDPE was measured as 0.944 ± 0.002 , 1.029 ± 0.02 and 1.054 ± 0.03 g/cm³, respectively. A single microparticle causes

Table 6 Physical and thermal properties of unfilled HDPE and micro- and nano-CaCO₃ particle-filled HDPE

Samples codes	Physical and thermal properties		
	Density (g/cm ³)	MFI (g/10 min)	VST (°C)
Unfilled HDPE	0.944 ± 0.002	0.262 ± 0.011	124.30 ± 0.99
Micro-CaCO ₃ /HDPE	1.054 ± 0.030	0.274 ± 0.014	123.43 ± 0.36
Nano-CaCO ₃ /HDPE	1.029 ± 0.020	0.321 ± 0.021	122.03 ± 0.37 [14]

larger pores in the HDPE matrix compared to a single nanoparticle. However, the total number of nano-CaCO₃ particles in the HDPE matrix filled with 10 wt% CaCO₃ is higher than the number of micro-CaCO₃ particles in the 10 wt% CaCO₃ microparticle-filled HDPE matrix. Therefore, the total pore volume in nanoparticle-filled HDPE is larger than that in microparticle-filled HDPE. As a result, the density of microparticle/HDPE is higher than that of nanoparticle/HDPE due to the low total pore volume. In addition, the nanoparticles generate a thinner polymer filament due to the high compression ratio.

The results of melt flow index (MFI) of filled and unfilled HDPE showed that the melt viscosity of both the filled HDPE matrices were higher than those of the unfilled HDPE. In addition, it was found that the MFI value of nanoparticle-filled HDPE is higher than microparticle-filled HDPE. The increase in MFI value indicates the increased motion of the HDPE chains. Also, the treatment of filler with quaternary ammonium or stearic acid produces a soft interphase [32] around each filler particle. Therefore, stearic acid-treated CaCO₃ filler particles in HDPE matrix acted as the plasticizer due to the soft interphase area around filler particle formed

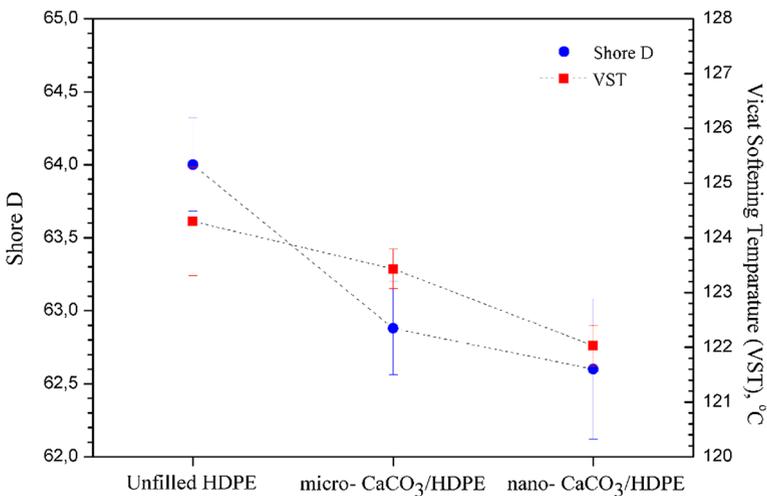


Fig. 8 Plots of vicat softening temperature values and Shore D hardness for the samples

by stearic acid treatment. It was concluded that the nanoparticle increased the mobility of polymer chains under heat and load according to the microparticle.

The values of VST and hardness measured for the samples are presented in Fig. 8. As shown in Table 6, the addition of both the filler particles decreased VST of unfilled HDPE. The decrease in VST may be associated with the samples' Shore D hardness values due to similar measurement principles (penetration of the test needle to the surface of the sample). As shown in Fig. 8, with the addition of micro- and nano- CaCO_3 , the hardness of the unfilled HDPE decreased. The reduction in the VST value with the addition of filler can be interpreted to be due to the decrease in the hardness of HDPE. This decrease trend in VST and hardness may be explained by the plasticizing effect of the soft interphase area around filler and low hardness of the CaCO_3 filler compared to unfilled HDPE. In addition, it was found that the nanoparticle is more effective at decreasing VST of unfilled HDPE as compared with the microparticle.

SEM, TEM and XRD characterizations

Characterizations of the phase of filled and unfilled HDPE were accomplished using XRD. The XRD patterns, which are characteristic for the CaCO_3 filler particles, unfilled HDPE and micro- and nano- CaCO_3 filled HDPE, are given in Fig. 9. The characteristic peak of CaCO_3 filler particle that is rhombohedral crystal lattice and unfilled HDPE which has a high degree of crystalline was determined at 30.52° and 23.49° , respectively. As shown in Fig. 9, the characteristic peak of the CaCO_3 filler particle in the filled HDPE matrix was detected as 32.05° . It can be interpreted that the micro- and nano- CaCO_3 particles were not adequately dispersed in HDPE matrix, according to this finding [14]. Figure 9 supports the nano- CaCO_3 dispersion findings in XRD study. As shown in Fig. 10a, the distribution of nano- CaCO_3 in the HDPE matrix is satisfactory, but it can be said that the nanoparticle dispersion is insufficient. The dispersion of inorganic nanofiller in a thermoplastic is a very difficult process. The dispersion level can be improved by surface modification of the nanofillers and appropriate processing conditions.

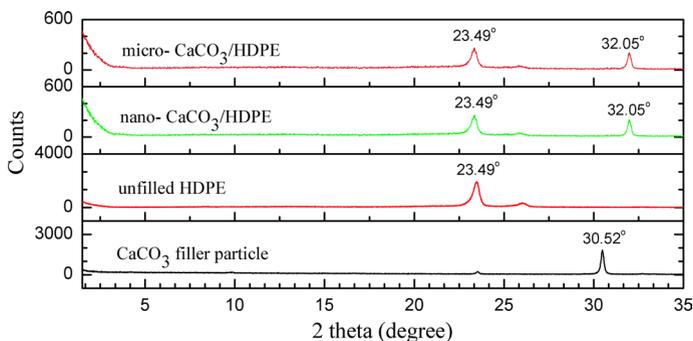


Fig. 9 XRD patterns for the CaCO_3 filler particle, unfilled HDPE and micro- and nano- CaCO_3 -filled HDPE

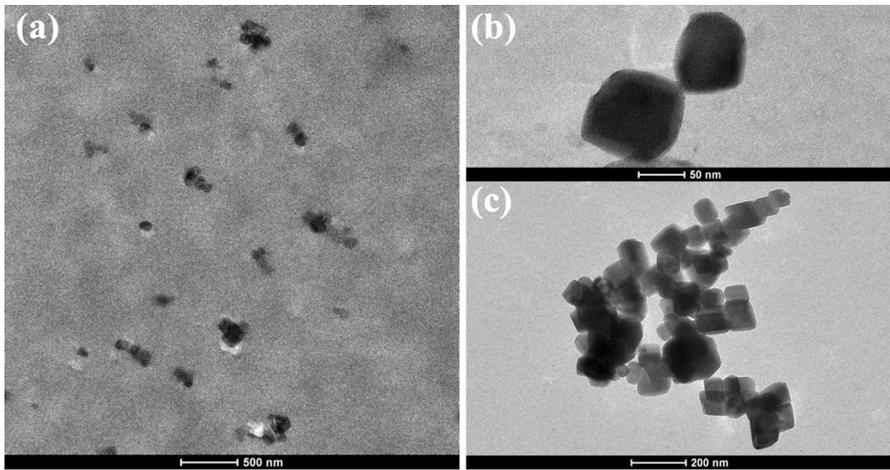


Fig. 10 TEM images of **a** the dispersion and distribution of nano- CaCO_3 particle in the HDPE matrix, **b** the nano- CaCO_3 particles with spherical morphology at 50 nm magnification and **c** the general image of the nano- CaCO_3 particles at 200-nm magnification

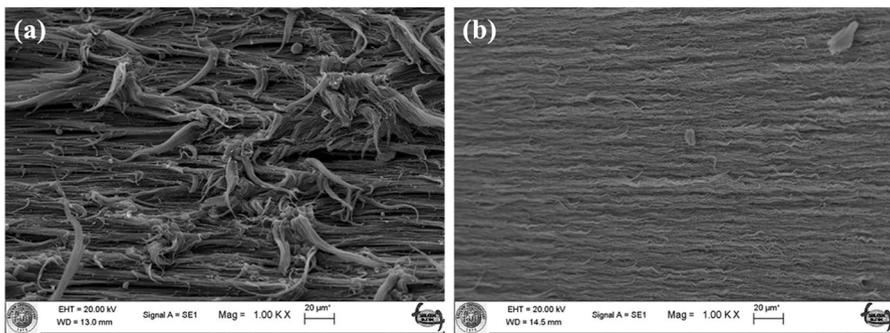


Fig. 11 The tensile surface of **a** micro- and **b** nano- CaCO_3 particle-filled HDPE in the necking zone

The fracture surface images of filled HDPE obtained by SEM showed that yield and plastic flow are accompanied by strong whitening in the necking zone of the filled HDPE. Figure 11 presents a typical SEM micrograph of stretched tensile surface of the filled HDPE. The reduction in the amount of plastic deformation of unfilled HDPE with the addition of fillers may be attributed to the higher rigidity of the micro- and nano- CaCO_3 filler particle, inducing a severe reduction in the elongations at break of unfilled HDPE, according to Fig. 2. In addition, the presence of extended fiber in Fig. 11 proves that the ductility of microparticle-filled HDPE is higher in contrast with the nanoparticle-filled HDPE. Impact fracture surface of filled and unfilled HDPE matrixes are given in Figs. 12, 13, and 14. These changes in the impact surface are similar to those reported previously by Sepet et al. [14, 26]. Herein, it was detected that the imperfection differences

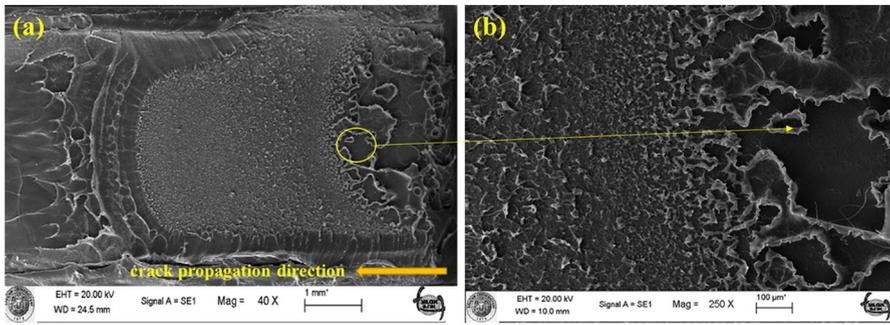


Fig. 12 The impact surface of the unfilled HDPE, **a** general impact surface image and **b** magnified image

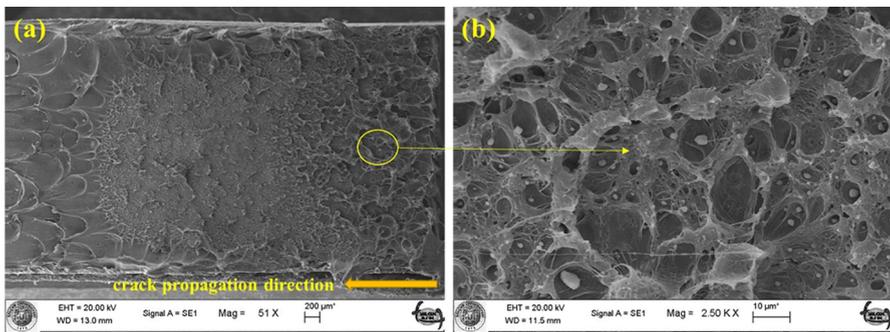


Fig. 13 The impact surface of micro- CaCO_3 particle-filled HDPE, **a** general impact surface image and **b** magnified image

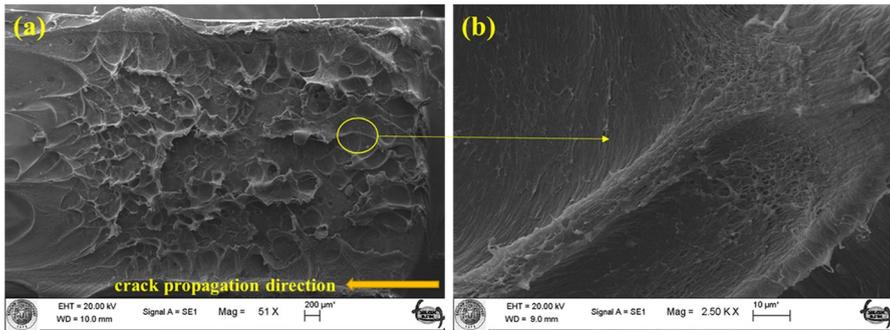


Fig. 14 The impact surface of nano- CaCO_3 particle-filled HDPE, **a** general impact surface image and **b** magnified image

bring impact in fracture surface due to particle size effect. Liu et al. emphasized that the toughening is probably not effective due to the agglomeration of CaCO_3 particles. The toughening mechanisms are related to the bond of particles. The

well-bonded particle to matrix suppresses the crazing of the polymer matrix and provides the formation of extensive plastic deformation [33, 34]. However, as shown in Fig. 13a, the excessive surface deformation of the impact surface of microparticle-filled HDPE was observed in contrast with nanoparticle-filled HDPE (see Fig. 13b). The elongated cavities around the debonded microparticles distinctly appear in Fig. 13b. It can be said that the ductile zone area of unfilled HDPE detected in Fig. 12b is decreased as compared to the microparticle-filled HDPE shown in Fig. 13b. However, the ductile zones were not observed in the impact fracture surface of nanoparticle-filled HDPE (see Fig. 14b), and the fracture surface was substantially transformed into a brittle from ductile characteristic as shown in Fig. 12b. According to the impact test results and SEM analysis, a parallelism was found in the decrease in the impact strength of filled HDPE with the increase in the brittle ratio of the impact fracture surfaces.

Conclusions

In this study, mechanical, thermal and creep behavior of unfilled HDPE and 10 wt% micro- and nano- CaCO_3 particles-filled HDPE matrixes were investigated using tensile, flexural, impact, creep, hardness, density, vicat softening temperature and melt flow index. The conclusions are summarized as follows.

1. The large filler particle size has a positive effect on the flexural modulus of the unfilled HDPE. The flexural modulus of the unfilled HDPE increased by 81% with the use of micro- CaCO_3 filler particle. However, tensile modulus of the unfilled HDPE increased by 5% with the use of nano- CaCO_3 filler particle. The different filler particle sizes have been effective on flexural and tensile modules.
2. The tensile and flexural strength almost remained unchanged with the addition of micro- and nanoparticles. The elongations at break of filled HDPE decrease significantly as compared to the unfilled HDPE.
3. It was found that nanoparticles reduce the static toughness of the unfilled HDPE by 54%, while microparticles reduce by 70%.
4. The filler particle/matrix interface of all spherical microparticles in matrix is smaller than that of nanoparticles for the same filler amount. When a load is applied to the microparticle-filled HDPE, the load transfer from the microparticle/matrix interface will cause debonding damage due to the small interface area.
5. The microparticles raised more the density of the unfilled HDPE as compared to nanoparticles.
6. It was concluded that both micro- and nano- CaCO_3 particles decrease the VST of the unfilled HDPE due to the plasticizing effect of the soft interphase area around the filler and low hardness of the filler.
7. It was found that the melt flow index of unfilled HDPE is higher than that of the unfilled and microparticle-filled HDPE.

8. It was revealed that the microparticle is more effective than the nanoparticle on creep behavior of the unfilled HDPE at 8 and 12 MPa stress levels. However, the nanoparticle improves more than the microparticle the creep behavior of the unfilled HDPE at the 16 MPa stress level.
9. It was observed that the impact strength of the filled HDPE samples decrease with the increase in the brittle ratio of the impact fracture surfaces discovered from SEM studies.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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